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| 14. ABSTRACT<br>The work explores the potential of AlN as an active material for deep UV optoelectronics device applications and to address doping issues in AlN and Al-rich AlGa <sub>N</sub> .  |                   |                                |                                  |   |   |
| 15. SUBJECT TERMS<br>III-nitride wide bandgap semiconductors; deep UV photonics; doping issues  |                   |                                |                                  |   |   |
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## Report Title

High Al-content AlGaIn alloys for deep UV laser applications

### ABSTRACT

The work explores the potential of AlN as an active material for deep UV optoelectronics device applications and to address doping issues in AlN and Al-rich AlGaIn.

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**Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:**

**(a) Papers published in peer-reviewed journals (N/A for none)**

| <u>Received</u> | <u>Paper</u> |
|-----------------|--------------|
|-----------------|--------------|

**TOTAL:**

**Number of Papers published in peer-reviewed journals:**

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**(b) Papers published in non-peer-reviewed journals (N/A for none)**

| <u>Received</u> | <u>Paper</u> |
|-----------------|--------------|
|-----------------|--------------|

**TOTAL:**

**Number of Papers published in non peer-reviewed journals:**

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**(c) Presentations**

1. "Semiconducting hexagonal boron nitride for deep ultraviolet photonics," SPIE-Photonic West - Conference on Quantum Sensing and Nanophotonic Devices IX, San Francisco, January 2012, invited.
2. "III-nitride micro- and nano-photonics," Delivered in Symposium EE of International Conference on Materials for Advanced Technologies, Singapore, June, 2011, invited.
3. "Nitride Semiconductors for Energy Generation," Delivered in Symposium EE of International Conference on Materials for Advanced Technologies, Singapore, June 2011, invited.
4. "Bright future of solid-state lighting," Royal Society Kan Tong Po Visiting Professorship Inaugural Public Lecture, Hong Kong Polytechnic University, July 2011, invited.
5. "III-Nitride Nano-structures for Energy Generation," Nano-Energy Workshop 2010: Nanotechnology for Energy Applications, Leigh University, Sept. 13-16, 2010, invited.
6. "III-Nitrides nanostructures for energy generation," SPIE-Photonic West - Conference on Quantum Sensing and Nanophotonic Devices VII, San Francisco, January 2010, invited.
7. "Nitride LEDs with Nanostructures and on Si Substrates," Indo-US Workshop on Visible & UV Sources for Solid-State Lighting & Water Purification, Anna University, Chennai, India, Jan. 2009, invited.
8. "Processes and Devices of GaN Materials on Si," 2008 Material Research Society Spring Meeting, Tutorial, San Francisco, April 2008, invited.

**Number of Presentations:** 0.00

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**Non Peer-Reviewed Conference Proceeding publications (other than abstracts):**

| <u>Received</u> | <u>Paper</u> |
|-----------------|--------------|
|-----------------|--------------|

**TOTAL:**

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Paper

TOTAL:

Patents Submitted

Patents Awarded

Awards

PI was also elected as the American Physical Society fellow in 2010 and PI was awarded Royal Society Kan Tong Po Visiting Professorship (through Hong Kong PolyU) in 2011.

Graduate Students

| <u>NAME</u>             | <u>PERCENT SUPPORTED</u> | Discipline |
|-------------------------|--------------------------|------------|
| New EntryRajendra Dahal | 0.50                     |            |
| New EntryBed Pantha     | 0.50                     |            |
| New EntryAshok Sedhain  | 0.50                     |            |
| <b>FTE Equivalent:</b>  | <b>1.50</b>              |            |
| <b>Total Number:</b>    | <b>3</b>                 |            |

Names of Post Doctorates

| <u>NAME</u>            | <u>PERCENT SUPPORTED</u> |  |
|------------------------|--------------------------|--|
| Jing Li                | 0.50                     |  |
| Sixuan Jin             | 0.50                     |  |
| <b>FTE Equivalent:</b> | <b>1.00</b>              |  |
| <b>Total Number:</b>   | <b>2</b>                 |  |

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### **Names of Faculty Supported**

| <u>NAME</u>            | <u>PERCENT SUPPORTED</u> | National Academy Member |
|------------------------|--------------------------|-------------------------|
| Hongxing Jiang         | 0.08                     |                         |
| Jingyu Lin             | 0.08                     |                         |
| <b>FTE Equivalent:</b> | <b>0.16</b>              |                         |
| <b>Total Number:</b>   | <b>2</b>                 |                         |

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### **Names of Under Graduate students supported**

| <u>NAME</u>            | <u>PERCENT SUPPORTED</u> |
|------------------------|--------------------------|
| <b>FTE Equivalent:</b> |                          |
| <b>Total Number:</b>   |                          |

### **Student Metrics**

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: .....

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:.....

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):.....

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:.....

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense .....

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: .....

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### **Names of Personnel receiving masters degrees**

| <u>NAME</u>          |
|----------------------|
| <b>Total Number:</b> |

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### **Names of personnel receiving PhDs**

| <u>NAME</u>          |
|----------------------|
| Rajendra Dahal       |
| Bed Pantha           |
| Ashok Sedhain        |
| <b>Total Number:</b> |

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### **Names of other research staff**

| <u>NAME</u>            | <u>PERCENT SUPPORTED</u> |
|------------------------|--------------------------|
| <b>FTE Equivalent:</b> |                          |
| <b>Total Number:</b>   |                          |

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**Sub Contractors (DD882)**

**Inventions (DD882)**

**Scientific Progress**

See attached

**Technology Transfer**

## Final Report

Funding No: W911NF-08-1-0375  
Project Title: High Al-content AlGa<sub>N</sub> alloys for deep UV laser applications  
PI Name: Hongxing Jiang & Jingyu Lin  
PI Address: Nanophotonics Center, Texas Tech University  
[Hx.jiang@ttu.edu](mailto:Hx.jiang@ttu.edu); [jingyu.lin@ttu.edu](mailto:jingyu.lin@ttu.edu)

### I. Summary of Progress

III-nitride wide bandgap semiconductors, with energy band gap varying from 0.9 eV (InN) to 3.4 eV (Ga<sub>N</sub>) to about 6.2 eV (AlN), have been recognized as technologically important materials. Photonic devices based on III-nitrides offer benefits including UV/blue emission; large band offsets of Ga<sub>N</sub>/AlN or InN/AlN heterostructures allowing novel quantum well (QW) device design, and inherently high emission efficiencies. Furthermore, due to their mechanical hardness and larger band gaps, III-nitride based devices may operate at much higher temperatures and voltages/power levels for any dimensional configuration and in harsher environments than other semiconductor devices and are expected to provide much lower temperature sensitivities, which are crucial advantages for many applications. AlGa<sub>N</sub> alloys with high Al contents, covering from 350 nm to 200 nm, cannot be replaced by any other semiconductor system due to the fact that no other semiconductor possesses such a large direct bandgap (diamond is 5.4 eV with indirect bandgap), as well as the ability of bandgap engineering through the use of alloying and heterostructure design. Efficient ultraviolet (UV) light sources/sensors are crucial in many fields of research. For instance, protein fluorescence is generally excited by UV light; monitoring changes of intrinsic fluorescence in a protein can provide important information on its structural changes.

However, there are many problems and questions that still stand in the way of the practical device implementation of UV photonic devices. Among these, the attainment of highly conductive p-type AlGa<sub>N</sub>, especially in high Al content AlGa<sub>N</sub> alloys, remains one of the biggest obstacles for the III-nitride research. Methods for improved material qualities, which would enhance the doping efficiencies and device performance, need to be further explored. The project explores the potential of AlN as an active material for deep UV optoelectronics device applications and to address doping issues in AlN and Al-rich AlGa<sub>N</sub>.

We highlight a few examples of our studies below:

#### ➤ High crystalline quality AlN epilayer growth technology development

We have carried out the growth and systematic studies of the optoelectronic and structural properties of AlN epilayers through the measurements of x-ray diffraction (XRD), photoluminescence (PL) and the dark current of the fabricated AlN DUV photodetectors. The results revealed that the threading dislocation (TD) density, in particular the edge TD density, decreases considerably with increasing the epilayer thickness. The FWHM of XRD rocking curves of the (002) and (102) reflections of a 4 μm epilayer are as small as 63 and 437 arcsec, respectively. These are among the smallest values reported for AlN epilayers and are even smaller than those of the best Ga<sub>N</sub> epilayers grown on sapphire (Ga<sub>N</sub> (002) reflection peak has a FWHM of about 150 arcsec).

From the tilt (out-of plane rotation) and twist (in-plane rotation) spread caused by the mosaicity of the AlN film, the dislocation density was estimated. The screw dislocation density was  $\sim 5 \times 10^6 \text{ cm}^{-2}$  in the 4  $\mu\text{m}$  thick AlN epilayer and is more than one order of magnitude lower than that in GaN of the same thickness ( $\sim 10^8 \text{ cm}^{-2}$ ). This clearly indicates that AlN epilayer is an effective dislocation filter. This reduction in screw dislocation density is particularly important for vertical optoelectronic devices such as LEDs, laser diodes (LDs), and Schottky detectors because screw dislocations are one of the major sources of current leakage paths, which increase with increasing current density. Screw dislocations also behave as non-radiative recombination centers that reduce the output intensity from optical devices.

➤ AlN as an active deep ultraviolet optoelectronics material

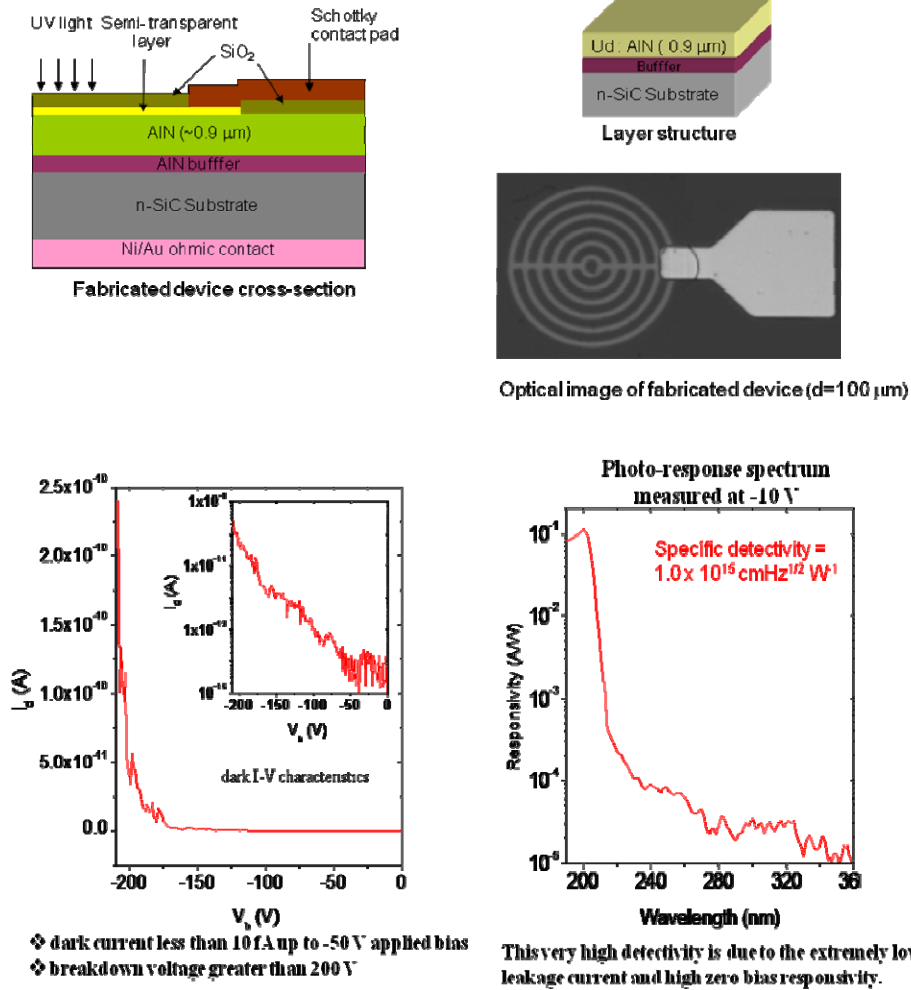


Fig. 1 Hybrid AlN-SiC deep UV Schottky barrier photodetectors

We have successfully fabricated deep UV Schottky barrier photodetectors by exploiting the epitaxial growth of high quality AlN epilayer on n-type SiC substrate (Fig. 1). The fabricated AlN/n-SiC hybrid Schottky barrier detectors exhibited a peak responsivity at 200 nm with very sharp cut off wavelength at 210 nm, very high reverse breakdown voltages ( $> 200 \text{ V}$ ), very low

dark currents (about 10 fA at a reverse bias of 50 V), and high responsivity and DUV to UV/visible rejection ratio. These outstanding features are direct attributes of the fundamental material properties and high quality of AlN epilayers. The fabricated photodetectors also have a thermal energy limited detectivity at zero bias of about  $1.0 \times 10^{15} \text{ cmHz}^{1/2} \text{ W}^{-1}$ . These results demonstrated that AlN epilayers are an excellent candidate as an active material for DUV optoelectronic device applications.

#### ➤ P-type doping limit in AlN and AlGaN

In Mg doped AlGaN alloys, native defects such as nitrogen vacancies, ( $V_N^{3+}$ ) and ( $V_N^{1+}$ ), limit *p*-type conductivity of AlGaN. Figure 3 below compares the 300 K PL spectra of (a) an undoped AlN epilayer, (b) a Mg-doped AlN epilayer with high resistivity, and (c) a Mg-doped AlN epilayer with measureable *p*-type conductivities (or reduced resistivities) at elevated temperatures. Undoped AlN has a strong band-edge emission peak at 5.98 eV due to the recombination of free excitons and exhibits virtually no impurity transitions in the low energy region, ensuring a good optical quality. AFM revealed an atomically smooth surface with a root mean square (RMS) roughness of about 7 Å within a 2 μm x 2 μm scan. These undoped AlN epilayers were employed as templates for the subsequent growth of Mg-doped AlN epilayers. For Mg-doped AlN epilayers, the PL spectra encompass an emission peak at around 4.7 eV, in addition to the band-edge emission at 5.94 eV. The band-edge emission peak at 5.94 eV is due to the recombination of excitons bound to neutral Mg acceptors (or acceptor-bound excitons  $I_1$ ). We have identified that the 4.7 eV emission line is related to nitrogen vacancies ( $V_N^{3+}$ ).

A clear correlation between the electrical and optical properties of Mg-doped AlN epilayers has been observed. Samples exhibiting strong emissions at 4.7 eV are generally highly insulating. Hall-effect measurements were carried out at elevated temperatures. The resistivity for one of our Mg-doped AlN epilayers, in which the intensity of nitrogen vacancy ( $V_N^{3+}$ ) related emission line at 4.7 eV was minimized, was measured in the temperature range between 400 and 900 K, from which an activation energy of about 0.5 eV for Mg acceptor in AlN was obtained.

Furthermore, by monitoring the  $V_N^{3+}$  related PL emission to the band edge emission intensity and *p*-type resistivity at elevated temperatures, we have confirmed *p*-type conduction in  $\text{Al}_{0.7}\text{Ga}_{0.3}\text{N}$  alloys at elevated temperatures and a *p*-type resistivity of about 40 Ω-cm at 800 K was observed. Although Mg doped AlGaN alloys with high Al contents are generally highly resistive at room temperature, our work has provided a more coherent picture for the conductivity control of AlGaN and AlN.

#### ➤ **Time-resolved photoluminescence studies of Be-doped AlN epilayers**

AlN epilayers with *n*-type conductivity with a reasonable free electron concentration ( $9.5 \times 10^{16}$  to  $7.4 \times 10^{17} \text{ cm}^{-3}$ ) have been obtained by Si doping by several groups, but the situation is quite challenging for *p*-type doping as we have demonstrated. Mg is the most commonly used *p*-type dopant in nitrides. The resistivity of Mg-doped AlGaN is found to increase with Al-content and becomes extremely high in Mg doped AlN ( $\sim 1 \text{ Ω-cm}$  in GaN to  $> 10^7 \text{ Ω-cm}$  in AlN at 300 K) due to increased activation energy of Mg ( $\sim 160$  in GaN vs. 510 meV in AlN). However, *p*-type conduction in Mg doped Al-rich AlGaN and pure AlN was observed only at elevated temperatures ( $> 700 \text{ K}$ ). With Mg doping limited by saturation, assuming a maximum attainable doping concentration of  $\sim 10^{20} \text{ cm}^{-3}$ , a maximum achievable free hole concentration (*p*) at room temperature in AlN would be only  $\sim 10^{12} \text{ cm}^{-3}$  ( $p = N_A e^{-E_0 / K_B T}$ , where  $N_A$  is the doping concentration and  $E_0 \sim 0.5 \text{ eV}$  the Mg activation energy), which may be further reduced by compensation. Previous calculations have predicted that Be occupying Al site ( $\text{Be}_{\text{Al}}$ ) in AlN acts



as an acceptor with a lower activation energy of  $\text{Be}_{\text{Al}}$  than Mg. The reduced activation energy of Be in AlN has the potential to partly address the p-type doping issue by increasing the room temperature free hole concentration. To date, no experimental results have been reported so far for Be doped AlN.

Be doped AlN epilayers have been grown by metal organic chemical vapor deposition and their optical properties have been studied by deep ultraviolet picosecond time-resolved photoluminescence spectroscopy. At 10K, Be acceptor-bound exciton transition has been observed at about 6.03 eV. The binding energy of excitons bound to Be acceptors in AlN is determined to be about 33 meV, which is about 8 meV smaller than that of Mg acceptor-bound exciton in AlN. The smaller binding energy of acceptor-bound exciton in Be doped AlN indicates a shallower acceptor level of Be than Mg in AlN in accordance with Haynes' rule. The measured PL decay lifetimes of the  $I_1$  transition in Be and Mg doped AlN (93 and 119 ps, respectively) also satisfy the established trend of decreased lifetime with decreasing binding energy of acceptor bound excitons. Our experimental data from temperature dependent PL and decay lifetime measurements of the  $I_1$  transition provided a coherent picture to support the fact that the Be energy level is shallower than that of Mg in AlN. However, as our Be doped AlN layers are highly resistive, direct transition from free electron to neutral Be acceptor couldn't be observed which would have provided a direct measure of the energy level of  $\text{Be}_{\text{Al}}$  acceptor in AlN. Much more work is required to obtain Be doped AlN epilayers that exhibit better p-type conductivity than that of Mg doped layers.

## II. Publications resulted from ARO support:

- A. Sedhain, T. M. Al Tahtamouni, J. Li, J. Y. Lin, and H. X. Jiang, "Beryllium acceptor binding energy in AlN," Appl. Phys. Lett. 93, 141104 (2008); [doi:10.1063/1.2996977](https://doi.org/10.1063/1.2996977).
- R. Dahal, J. Li, Z. Y. Fan, M. L. Nakarmi, T. M. Al Tahtamouni, J. Y. Lin, and H. X. Jiang, "AlN MSM and Schottky photodetectors," phys. stat. sol. (c) 5, No. 6 (2008); [doi:10.1002/pssc.200778489](https://doi.org/10.1002/pssc.200778489).
- B. N. Pantha, A. Sedhain, J. Li, J. Y. Lin, and H. X. Jiang, "Probing the relationship between structural and optical properties of Si-doped AlN," Appl. Phys. Lett. 96, 131906 (2010); [doi:10.1063/1.3374444](https://doi.org/10.1063/1.3374444).
- A. Sedhain, J. Y. Lin, and H. X. Jiang "AlN: Properties and Applications," Chapter 2 in "*Handbook of Luminescent Semiconductor Materials*," edited by L. Bergman and L. McHale, published in September, 2011 by CRC Press, Taylor & Francis Group (ISBN-13: 978-1439834671).
- J. Li, J. Y. Lin, H. X. Jiang, and N. Sawaki, "III-Nitrides on Si Substrates," Book Chapter 3 in "*III-V Compound Semiconductors: Integration with Silicon-Based Microelectronics*," edited by T. Li, M. Mastro and A. Dadgar, published by CRC Press (Boca Raton 2010); (ISBN-13: 978-1-4398-1523-6).
- B.N. Pantha, J. Y. Lin, and H. X. Jiang, "Growth and properties of Al-rich AlGaN," Book chapter in "*Advances in GaN and ZnO-based Thin Film, Bulk and Nanostructured Materials and Devices*," ed S.J. Pearton, to be published by Springer; (ISBN: 978-3-642-23520-7).